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Entitled:

NOVEL COUPLER FOR USE IN OXIDATIVE HAIR DYEING

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NOVEL COUPLER FOR USE IN OXIDATIVE HAIR DYEING

Field of the Invention

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This invention relates to novel couplers for use in hair coloring compositions comprising one or more oxidative hair coloring agents in combination with one or more oxidizing agents. The invention also relates to hair coloring compositions of these novel couplers and to coloring or dyeing of hair using compositions containing these couplers.

Background of the Invention

Coloration of hair is a procedure practiced from antiquity employing a variety of means. In modern times, the most extensively used method employed to color hair is to color hair by an oxidative dyeing process employing hair coloring systems utilizing one or more oxidative hair coloring agents in combination with one or more oxidizing agents.

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Most commonly a peroxy oxidizing agent is used in combination with one or more oxidative hair coloring agents, generally small molecules capable of diffusing into hair and comprising one or more primary intermediates and one or more couplers. In this procedure, a peroxide material, such as hydrogen peroxide, is employed to activate the small molecules of primary intermediates so that they react with couplers to form larger sized compounds in the hair shaft to color the hair in a variety of shades and colors.

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A wide variety of primary intermediates and couplers have been employed in such oxidative hair coloring systems and compositions. Among the primary

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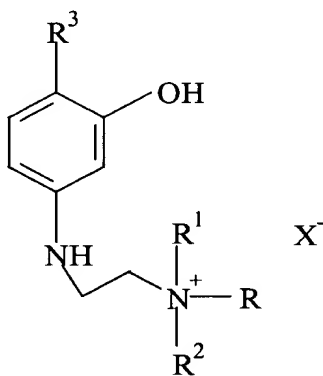
intermediates employed there may be mentioned p-phenylenediamine, p-toluenediamine, p-aminophenol, 4-amino-3-methylphenol, and as couplers there may be mentioned resorcinol, 2-methylresorcinol, 3-aminophenol, and 5-amino-2-methylphenol. A majority of the shades have been produced with dyes based on p-phenylenediamine.

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For providing an orange coloration to hair 2-methyl-5-aminophenol has been extensively used in combination with p-aminophenol as a primary intermediate. However, the resulting orange color on hair undergoes significant changes on exposure to light or shampooing. US Patent No. 4,065,255 and EP patent publications EP 634165 A1 and EP 667143 A1 suggest the use of 2-methyl-5-N-hydroxyethylaminophenol, 2-methyl-5-alkylaminophenol and 2-methyl-5-aminophenol as couplers. Therefore, there is a need for new orange couplers for use in oxidative hair dyeing compositions and systems.

Brief Summary of the Invention

This invention provides novel couplers of the formula (1):



(1)

wherein X is selected from halogen where the halogen is preferably Cl, Br or I; R³ is selected from C₁ to C₂ alkyl and hydroxyethyl; and R, R¹ and R² are each independently selected from C₁ to C₂₂ alkyl or C₁ to C₂₂ mono or dihydroxyalkyl groups or two of R, R¹ and R² together with the nitrogen atom to which they are

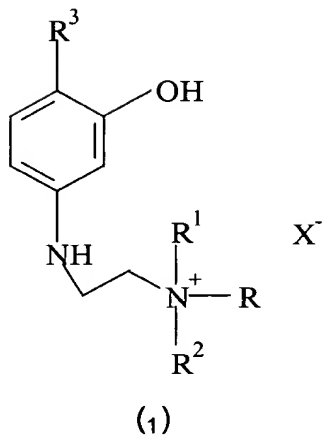
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attached form a C₃ to C₆ cycloaliphatic or a C₃ to C₁₄ aromatic group, the cycloaliphatic or aromatic group optionally containing in their rings one or more hetero atoms selected from O, S and N atoms. These novel couplers are used to provide coloration to hair in which there is good dye uptake by the hair and provides shades or colors which are stable over a relatively long period of time. The novel couplers provide for dyeing of hair that provides color or shades that possess good wash fastness and do not undergo the significant changes on exposure to light or shampooing as experienced with 2-methyl-5-aminophenol.

Detailed Description of the Invention

Preferred coupler compounds of this invention are those of formula (1)



wherein X is Cl, Br or I; R³ is methyl, ethyl or hydroxyethyl; and two of R, R¹ and R² together with the nitrogen atom to which they are attached form an C₃ to C₆ cycloaliphatic or C₃ to C₆ aromatic group optionally containing in the ring another N atom.

Especially preferred couplers of this invention are the following compounds:

1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;

1-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;

1-[2-(3-hydroxy-4-hydroxyethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;

1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium bromide;

5 1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium iodide;

1-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium propyl sulfate;

N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;

N-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;

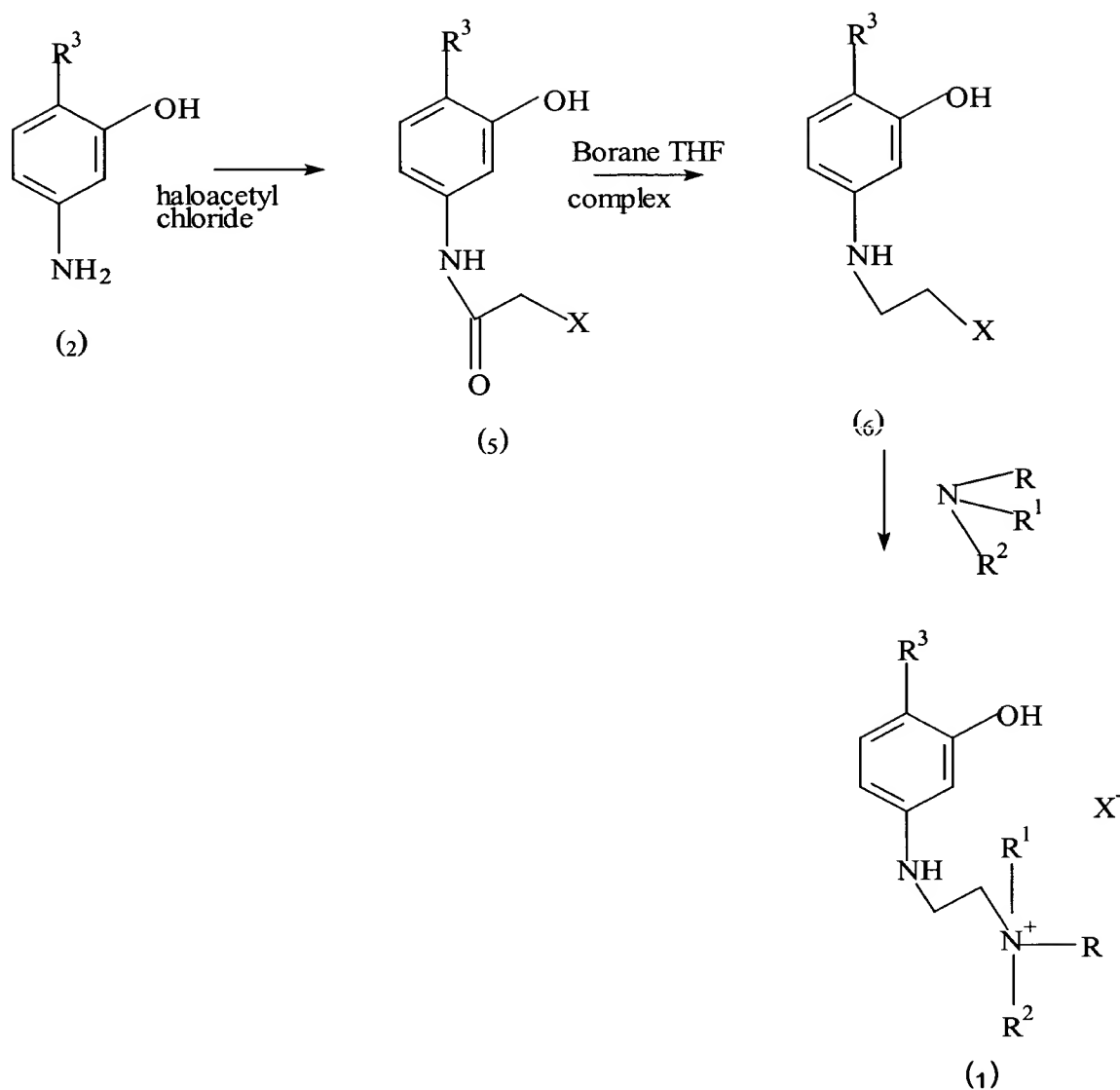
N-[2-(3-hydroxy-4-hydroxyethyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;

N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium bromide;and

N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium iodide.

The compounds of formula (1) of this invention are readily prepared according to the following reaction sequence.

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In the reaction sequence a solution of an aminophenol of formula (2) in tetrahydrofuran (THF) is added to a solution of haloacetyl chloride to produce a compound of formula (5). Treatment of the compound of formula (5) with a borane-THF complex produces a compound of formula (6) and reaction of this compound of formula (6) with a quaternization reagent of the formula $\text{N(R}^1\text{)(R}^2\text{)(R}^3\text{)}$ produces a compound of formula (1).

Synthesis Examples 1-10

Employing the appropriate aminophenol, haloacetylchloride, and N(R1)(R2)(R3) quaternization reagent in the forgoing described synthesis procedure the following coupler compounds of this invention are prepared.

1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;
N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;
1-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;
1-[2-(3-hydroxy-4-hydroxyethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;
1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium bromide;
1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium iodide;
N-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;
N-[2-(3-hydroxy-4-hydroxyethyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;
N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium bromide; and
N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium iodide.

Hair coloring compositions of this invention can contain the novel couplers of this invention as the sole coupler or can also contain other couplers in combination with primary intermediates.

For hair coloring compositions of this invention, there may be used one or more suitable primary intermediates in combination with the novel couplers of this invention. Suitable primary intermediates include, for example,

p-phenylenediamine derivatives such as: benzene-1,4-diamine (commonly known as p-phenylenediamine), 2-methyl-benzene-1,4-diamine, 2-chloro-benzene-1,4-diamine, N-phenyl-benzene-1,4-diamine, N-(2-ethoxyethyl)benzene-1,4-diamine, 2-[(4-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, (commonly known as

N,N-bis(2-hydroxyethyl)-p-phenylenediamine) (2,5-diamino-phenyl)-methanol, 1-(2,5-diamino-phenyl)-ethanol, 2-(2,5-diamino-phenyl)-ethanol, N-(4-aminophenyl)benzene-1,4-diamine, 2,6-dimethyl-benzene-1,4-diamine, 2-isopropyl-benzene-1,4-diamine, 1-[(4-aminophenyl)amino]-propan-2-ol, 2-propyl-benzene-1,4-diamine, 1,3-bis[(4-aminophenyl)(2-hydroxyethyl)amino]propan-2-ol, N⁴,N⁴,2-trimethylbenzene-1,4-diamine, 2-methoxy-benzene-1,4-diamine, 1-(2,5-diaminophenyl)ethane-1,2-diol, 2,3-dimethyl-benzene-1,4-diamine, N-(4-amino-3-hydroxy-phenyl)-acetamide, 2,6-diethylbenzene-1,4-diamine, 2,5-dimethylbenzene-1,4-diamine, 2-thien-2-ylbenzene-1,4-diamine, 2-thien-3-ylbenzene-1,4-diamine, 2-pyridin-3-ylbenzene-1,4-diamine, 1,1'-biphenyl-2,5-diamine, 2-(methoxymethyl)benzene-1,4-diamine, 2-(aminomethyl)benzene-1,4-diamine, 2-(2,5-diaminophenoxy)ethanol, N-[2-(2,5-diaminophenoxy)ethyl]-acetamide, N,N-dimethylbenzene-1,4-diamine, N,N-diethylbenzene-1,4-diamine, N,N-dipropylbenzene-1,4-diamine, 2-[(4-aminophenyl)(ethyl)amino]ethanol, 2-[(4-amino-3-methyl-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, N-(2-methoxyethyl)-benzene-1,4-diamine, 3-[(4-aminophenyl)amino]propan-1-ol, 3-[(4-aminophenyl)-amino]propane-1,2-diol, N-{4-[(4-aminophenyl)amino]butyl}benzene-1,4-diamine, and 2-[2-(2-{[(2,5-diaminophenyl)-oxy]ethoxy}ethoxy)ethoxy]benzene-1,4-diamine;

p-aminophenol derivatives such as: 4-amino-phenol (commonly known as p-aminophenol), 4-methylamino-phenol, 4-amino-3-methyl-phenol, 4-amino-2-hydroxymethyl-phenol, 4-amino-2-methyl-phenol, 4-amino-2-[(2-hydroxy-ethylamino)-methyl]-phenol, 4-amino-2-methoxymethyl-phenol, 5-amino-2-hydroxy-benzoic acid, 1-(5-amino-2-hydroxy-phenyl)-ethane-1,2-diol, 4-amino-2-(2-hydroxy-ethyl)-phenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-3-fluoro-phenol, 4-amino-2-(aminomethyl)-phenol, and 4-amino-2-fluoro-phenol;

o-aminophenol derivatives such as: 2-amino-phenol (commonly known as o-aminophenol), 2,4-diaminophenol, 2-amino-5-methyl-phenol, 2-amino-6-methyl-phenol, N-(4-amino-3-hydroxy-phenyl)-acetamide, and 2-amino-4-methyl-phenol; and

heterocyclic derivatives such as: pyrimidine-2,4,5,6-tetramine (commonly known as 2,4,5,6-tetraaminopyridine), 1-methyl-1H-pyrazole-4,5-diamine, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol, N²,N²-dimethyl-pyridine-2,5-diamine, 2-[(3-amino-6-methoxypyridin-2-yl)amino]ethanol, 6-methoxy-N²-methyl-pyridine-2,3-diamine, 2,5,6-triaminopyrimidin-4(1H)-one, pyridine-2,5-diamine, 1-isopropyl-1H-pyrazole-4,5-diamine, 1-(4-methylbenzyl)-1H-pyrazole-4,5-diamine, 1-(benzyl)-1H-pyrazole-4,5-diamine and 1-(4-chlorobenzyl)-1H-pyrazole-4,5-diamine.

The couplers of formula (1) of this invention may be used with any suitable coupler(s) in hair coloring compositions or systems of this invention.

Suitable known couplers include, for example:

phenols, resorcinol and naphthol derivatives such as: naphthalene-1,7-diol, benzene-1,3-diol, 4-chlorobenzene-1,3-diol, naphthalen-1-ol, 2-methylnaphthalen-1-ol, naphthalene-1,5-diol, naphthalene-2,7-diol, benzene-1,4-diol, 2-methylbenzene-1,3-diol, 7-amino-4-hydroxy-naphthalene-2-sulfonic acid, 2-isopropyl-5-methylphenol, 1,2,3,4-tetrahydro-naphthalene-1,5-diol, 2-chloro-benzene-1,3-diol, 4-hydroxy-naphthalene-1-sulfonic acid, benzene-1,2,3-triol, naphthalene-2,3-diol, 5-dichloro-2-methylbenzene-1,3-diol, 4,6-dichlorobenzene-1,3-diol, and 2,3-dihydroxy-[1,4]naphthoquinone;

m-phenylenediamines such as: 2,4-diaminophenol, benzene-1,3-diamine, 2-(2,4-diamino-phenoxy)-ethanol, 2-[(3-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, 2-methylbenzene-1,3-diamine, 2-[[2-(2,4-diamino-phenoxy)-ethyl]-(2-hydroxy-ethyl)-amino]-ethanol, 4-{3-[(2,4-diaminophenyl)oxy]propoxy}benzene-1,3-diamine, 2-(2,4-diamino-phenyl)-ethanol, 2-(3-amino-4-methoxy-phenylamino)-ethanol, 4-(2-amino-ethoxy)-benzene-1,3-diamine, (2,4-diamino-phenoxy)-acetic acid, 2-[2,4-diamino-5-(2-hydroxy-ethoxy)-phenoxy]-ethanol, 4-ethoxy-6-methylbenzene-1,3-diamine, 2-(2,4-diamino-5-methyl-phenoxy)-ethanol, 4,6-dimethoxybenzene-1,3-

diamine, 2-[3-(2-hydroxy-ethylamino)-2-methyl-phenylamino]-ethanol, 3-(2,4-diamino-phenoxy)-propan-1-ol, N-[3-(dimethylamino)phenyl]urea, 4-methoxy-6-methylbenzene-1,3-diamine, 4-fluoro-6-methylbenzene-1,3-diamine, 2-({3-[(2-hydroxyethyl)amino]-4,6-dimethoxyphenyl}-amino)ethanol, 3-(2,4-diaminophenoxy)-propane-1,2-diol, 2-[2-amino-4-(methylamino)-phenoxy]ethanol, 2-[(5-amino-2-ethoxy-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, 2-[(3-aminophenyl)amino]ethanol, N-(2-aminoethyl)benzene-1,3-diamine, 4-[(2,4-diamino-phenyl)oxy]methoxy}-benzene-1,3-diamine, and 2,4-dimethoxybenzene-1,3-diamine;

m-aminophenols such as: 3-amino-phenol, 2-(3-hydroxy-4-methyl-phenylamino)-acetamide, 2-(3-hydroxy-phenylamino)-acetamide, 5-amino-2-methyl-phenol, 5-(2-hydroxy-ethylamino)-2-methyl-phenol, 5-amino-2,4-dichloro-phenol, 3-amino-2-methyl-phenol, 3-amino-2-chloro-6-methyl-phenol, 5-amino-2-(2-hydroxy-ethoxy)-phenol, 2-chloro-5-(2,2,2-trifluoro-ethylamino)-phenol, 5-amino-4-chloro-2-methyl-phenol, 3-cyclopentylamino-phenol, 5-[(2-hydroxyethyl)amino]-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 3-(dimethylamino)phenol, 3-(diethylamino)phenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichloro-phenol, 3-[(2-methoxyethyl)amino]phenol, 3-[(2-hydroxyethyl)amino]phenol, 5-amino-2-ethyl-phenol, 5-amino-2-methoxyphenol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(3-hydroxy-2-methylphenyl)-amino]propane-1,2-diol, and 3-[(2-hydroxyethyl)amino]-2-methylphenol; and

heterocyclic derivatives such as: 3,4-dihydro-2H-1,4-benzoxazin-6-ol, 4-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 6-methoxyquinolin-8-amine, 4-methylpyridine-2,6-diol, 2,3-dihydro-1,4-benzodioxin-5-ol, 1,3-benzodioxol-5-ol, 2-(1,3-benzodioxol-5-ylamino)ethanol, 3,4-dimethylpyridine-2,6-diol, 5-chloropyridine-2,3-diol, 2,6-dimethoxypyridine-3,5-diamine, 1,3-benzodioxol-5-amine, 2-[[3,5-diamino-6-(2-hydroxy-ethoxy)-pyridin-2-yl]oxy]-ethanol, 1H-indol-4-ol, 5-amino-2,6-dimethoxypyridin-3-ol, 1H-indole-5,6-diol, 1H-indol-7-ol, 1H-indol-5-ol, 1H-indol-6-ol, 6-bromo-1,3-benzodioxol-5-ol, 2-aminopyridin-3-ol, pyridine-2,6-diamine, 3-[(3,5-

diaminopyridin-2-yl)oxy]propane-1,2-diol, 5-[(3,5-diaminopyridin-2-yl)oxy]pentane-1,3-diol, 1H-indole-2,3-dione, indoline-5,6-diol, 3,5-dimethoxypyridine-2,6-diamine, 6-methoxypyridine-2,3-diamine, and 3,4-dihydro-2H-1,4-benzoxazin-6-amine.

5 Preferred primary intermediates include:

p-phenylenediamine derivatives such as: 2-methyl-benzene-1,4-diamine, benzene-1,4-diamine, 1-(2,5-diamino-phenyl)-ethanol, 2-(2,5-diamino-phenyl)-ethanol, N-(2-methoxyethyl)benzene-1,4-diamine, 2-[(4-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol, and 1-(2,5-diaminophenyl)ethane-1,2-diol;

p-aminophenol derivatives such as 4-amino-phenol, 4-methylamino-phenol, 4-amino-3-methyl-phenol, 4-amino-2-methoxymethyl-phenol, and 1-(5-amino-2-hydroxy-phenyl)-ethane-1,2-diol;

o-aminophenol derivatives such as: 2-amino-phenol, 2-amino-5-methyl-phenol, 2-amino-6-methyl-phenol, N-(4-amino-3-hydroxy-phenyl)-acetamide, and 2-amino-4-methyl-phenol;

20 heterocyclic derivatives such as: pyrimidine-2,4,5,6-tetramine, 1-methyl-1H-pyrazole-4,5-diamine, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol, 1-(4-methylbenzyl)-1H-pyrazole-4,5-diamine, 1-(benzyl)-1H-pyrazole-4,5-diamine and N²,N²-dimethylpyridine-2,5-diamine.

25 Preferred couplers include:

phenols, resorcinol and naphthol derivatives such as: naphthalene-1,7-diol, benzene-1,3-diol, 4-chlorobenzene-1,3-diol, naphthalen-1-ol, 2-methyl-naphthalen-1-ol, naphthalene-1,5-diol, naphthalene-2,7-diol, benzene-1,4-diol, 2-methyl-benzene-1,3-diol, and 2-isopropyl-5-methylphenol;

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m-phenylenediamines such as: benzene-1,3-diamine, 2-(2,4-diaminophenoxy)-ethanol, 4-{3-[(2,4-diaminophenyl)oxy]propoxy}benzene-1,3-diamine, 2-(3-amino-4-methoxy-phenylamino)-ethanol, 2-[2,4-diamino-5-(2-hydroxy-ethoxy)-phenoxy]-ethanol, and 3-(2,4-diamino-phenoxy)-propan-1-ol;

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m-aminophenols such as: 3-amino-phenol, 5-amino-2-methyl-phenol, 5-(2-hydroxy-ethylamino)-2-methyl-phenol, and 3-amino-2-methyl-phenol; and

heterocyclic derivatives such as: 3,4-dihydro-2H-1,4-benzoxazin-6-ol, 4-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 1,3-benzodioxol-5-ol, 1,3-benzodioxol-5-amine, 1H-indol-4-ol, 1H-indole-5,6-diol, 1H-indol-7-ol, 1H-indol-5-ol, 1H-indol-6-ol, 1H-indole-2,3-dione, pyridine-2,6-diamine, and 2-aminopyridin-3-ol.

Most preferred primary intermediates include:

p-phenylenediamine derivatives such as: 2-methyl-benzene-1,4-diamine, benzene-1,4-diamine, 2-(2,5-diamino-phenyl)-ethanol, 1-(2,5-diamino-phenyl)-ethanol, and 2-[(4-amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol;

p-aminophenol derivatives such as: 4-amino-phenol, 4-methylamino-phenol, 4-amino-3-methyl-phenol, and 1-(5-amino-2-hydroxy-phenyl)-ethane-1,2-diol;

o-aminophenols such as: 2-amino-phenol, 2-amino-5-methyl-phenol, 2-amino-6-methyl-phenol, and N-(4-amino-3-hydroxy-phenyl)-acetamide; and

heterocyclic derivatives such as: pyrimidine-2,4,5,6-tetramine, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol, 1-(4-methylbenzyl)-1H-pyrazole-4,5-diamine, and 1-(benzyl)-1H-pyrazole-4,5-diamine.

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Most preferred couplers include:

phenols, resorcinol and naphthol derivatives such as: benzene-1,3-diol, 4-chlorobenzene-1,3-diol, naphthalen-1-ol, 2-methyl-naphthalen-1-ol, and 2-methyl-benzene-1,3-diol;

m-phenylenediamine such as: 2-(2,4-diamino-phenoxy)-ethanol, 2-(3-amino-4-methoxy-phenylamino)-ethanol, 2-[2,4-diamino-5-(2-hydroxy-ethoxy)-phenoxy]-ethanol, and 3-(2,4-diamino-phenoxy)-propan-1-ol;

m-aminophenols such as: 3-amino-phenol, 5-amino-2-methyl-phenol, 5-(2-hydroxy-ethylamino)-2-methyl-phenol, and 3-amino-2-methyl-phenol; and

heterocyclic derivatives such as: 3,4-dihydro-2H-1,4-benzoxazin-6-ol, 4-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 1H-indol-6-ol, and 2-aminopyridin-3-ol.

Understandably, the coupler compounds and the primary intermediate compounds, as well as the other dye compounds, in so far as they are bases, can be used as free bases or in the form of their physiologically compatible salts with organic or inorganic acids, such as hydrochloric acid or sulfuric acid, or, in so far as they have aromatic OH groups, in the form of their salts with bases, such as alkali phenolates.

The total amount of the combination of dye precursors (e.g., primary intermediate and coupler compounds) in the hair coloring compositions or systems of this invention is generally from about 0.001 to about 10, preferably from about 0.02 to about 10, and most preferably from about 0.2 to about 6.0 weight percent based on the total weight of the hair coloring composition. The primary intermediate and coupler compounds are generally used in equivalent amounts. However, it is possible

to use the primary intermediate compounds in either excess or deficiency, i.e., a molar ratio of primary intermediate to coupler generally ranging from about 5:1 to about 1:5.

5 The hair coloring compositions of this invention will contain the couplers of this invention in an effective coloring amount, generally in an amount of from about 0.001 to about 6 weight percent by weight of the hair dye composition, preferably from about 0.01 to about 3.5 weight percent. Other couplers, when present, are typically present in an amount such that in aggregate the concentration of couplers in the composition is from about 0.01 to about 6 weight percent. The primary intermediate(s) is present in an effective dyeing concentration generally an amount of from about 0.001 to about 6.0 weight percent by weight of the hair dye composition, preferably from about 0.01 to about 3.5 weight percent. Any suitable carrier or vehicle, generally an aqueous or hydroalcoholic solution, can be employed, preferably an aqueous solution. The carrier or vehicle will generally comprise up to about 40 weight percent.

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15 The hair coloring compositions of this invention may contain one or more cationic, anionic or amphoteric surface active agents, perfumes, antioxidants, sequestering agents, thickening agents, alkalizing or acidifying agents, and other dyeing agents.

20 The compositions of the present invention are used by admixing them with a suitable oxidant, which reacts with the hair dye precursors to develop the hair dye. Any suitable peroxide providing agent can be employed in the coloring compositions of this invention, particularly hydrogen peroxide (H_2O_2) or precursors therefor. Also suitable are urea peroxide, sodium perborate, sodium percarbonate, and melamine peroxide.

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30 Moreover, cosmetic additive ingredients, which are commonly used in compositions for coloring hair, can be used in the hair coloring compositions according to the invention, for example antioxidants, such as ascorbic acid, thioglycolic acid or

sodium sulfite, and perfume oils, complex formers, wetting agents, emulsifiers, thickeners and care materials.

5 The form of the hair coloring compositions according to the invention can be, for example, a solution, especially an aqueous or aqueous-alcoholic solution. However, the form that is particularly preferred is a cream, gel or an emulsion. Its composition is a mixture of the dye ingredients with the conventional cosmetic additive ingredients suitable for the particular preparation.

Conventional cosmetic additive ingredients in solutions, creams, emulsion or gels include, for example:

15 Solvents: In addition to water, solvents that can be used are lower alkanols (e.g., ethanol, propanol, isopropanol); polyols (e.g., carbitols, propylene glycol, glycerin). Under suitable processing, higher alcohols, such as cetyl alcohol, are suitable organic solvents, provided they are first liquified by melting, typically at low temperature (50 to 80 °C), before incorporation of other, usually lipophilic, materials. See WO 98/27941 (section on diluents) incorporated by reference.

20 Anionic and Nonionic Surfactants: These materials are from the classes of anionic, cationic, amphoteric or nonionic surfactant compounds, such as fatty alcohol sulfates, ethoxylated fatty alcohol sulfates, alkylsulfonates, alkylbenzensulfonates, alkyltrimethylammonium salts, alkylbetaines, ethoxylated fatty alcohols, ethoxylated nonylphenols, fatty acid alkanol amides and ethoxylated fatty acid esters. They are included for various reasons, e.g., to assist in thickening, for forming emulsions, to help in wetting hair during application of the hair dye composition, etc. Suitable materials are alkyl sulfates, ethoxylated alkyl sulfates, alkyl glyceryl ether sulfonates, methyl acyl taurates, acyl isethionates, alkyl ethoxy carboxylates, fatty acid mono-

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and diethanolamides. Reference is made to WO 98/52523 published November 26, 1998 and incorporated herein by reference.

Thickeners: Suitable thickeners include such as higher fatty alcohols, starches, cellulose derivatives, petrolatum, paraffin oil, fatty acids and anionic and nonionic polymeric thickeners based on polyacrylic and polyurethane polymers. Examples are hydroxyethyl cellulose, hydroxymethylcellulose and other cellulose derivatives, hydrophobically modified anionic polymers and nonionic polymers, particularly such polymers having both hydrophilic and hydrophobic moieties (i.e., amphiphilic polymers). Useful nonionic polymers include polyurethane derivatives such as PEG-150/stearyl alcohol/SDMI copolymer and PEG-150/stearyl alcohol SDMI copolymer. Other useful amphiphilic polymers are disclosed in US Pat. No. 6010541 incorporated by reference. Examples of anionic polymers that can be used as thickeners are acrylates copolymer, acrylates/ceteth-20 methacrylates copolymer, acrylates/ceteth-20 itaconate copolymer, and acrylates/behenteth-25 acrylates copolymer. Aculyn® polymers sold by Rohm & Haas, as well as hair care materials, such as cationic resins, lanolin derivatives, cholesterol, pantothenic acids and betaine.

Alkalizing agents: Suitable materials that are used to increase pH of the hair dye compositions include ammonia, aminomethylpropanol, methylethanolamine, triethanolamine and ethanolamine.

Conditioners: Suitable materials include silicones and silicone derivatives; hydrocarbon oils; monomeric quaternary compounds, and quaternized polymers. Monomeric quaternary compounds are typically cationic compounds, but may also include betaines and other amphoteric and zwitterionic materials. Suitable monomeric quaternary compounds include behentrialkonium chloride, behentrimonium chloride, benzalkonium bromide or chloride, benzyl triethyl ammonium chloride, bis-hydroxyethyl tallowmonium chloride, C12-18 dialkyldimonium chloride, cetalkonium chloride, cetearrimonium bromide and chloride, cetrimonium bromide, chloride and methosulfate, cetylpyridonium chloride, cocamidopropyl

ethyldimonium ethosulfate, cocamidopropyl ethosulfate, coco-ethyldimonium ethosulfate, cocotrimonium chloride and ethosulfate, dibehenyl dimonium chloride, dicetyldimonium chloride, dicocodimonium chloride, dilauryl dimonium chloride, disoydimonium chloride, ditallowdimonium chloride, hydrogenated tallow trimonium chloride, hydroxyethyl cetyl dimonium chloride, myristalkonium chloride, olealkonium chloride, soyethomonium ethosulfate, soytrimonium chloride, stearalkonium chloride, and many other compounds. See WO 98/27941 incorporated by reference. Quaternized polymers are typically cationic polymers, but may also include amphoteric and zwitterionic polymers. Useful polymers are exemplified by polyquaternium-4, polyquaternium-6, polyquaternium-7, polyquaternium-8, polyquaternium-9, polyquaternium-10, polyquaternium-22, polyquaternium-32, polyquaternium-39, polyquaternium-44 and polyquaternium-47. Silicones suitable to condition hair are dimethicone, amodimethicone, dimethicone copolyol and dimethiconol. See also WO 99/34770 published July 15, 1999, incorporated by reference, for suitable silicones. Suitable hydrocarbon oils would include mineral oil.

Natural ingredients: For example, protein derivatives, aloe, camomile and henna extracts.

Other adjuvants include acidulents to lower pH, buffers, chelating agents antioxidants, sequestrants, etc. These classes of materials and other species of materials in the classes referred to above but not specifically identified that are suitable are listed in the International Cosmetics Ingredient Dictionary and Handbook, (Eighth Edition) published by The Cosmetics, Toiletry, and Fragrance Association, incorporated by reference. In particular reference is made to Volume 2, Section 3 (Chemical Classes) and Section 4 (Functions) are useful in identifying a specific adjuvant/excipient to achieve a particular purpose or multipurpose.

The above-mentioned conventional cosmetic ingredients are used in amounts suitable for their purposes. For example the wetting agents and emulsifiers are used in concentrations of from about 0.5 to 30 percent by weight, the thickeners

are used in an amount of from about 0.1 to 25 percent by weight and the hair care materials are used in concentrations of from about 0.1 to 5.0 percent by weight.

5 The hair coloring compositions according to the invention can be weakly acidic, neutral or alkaline according to their composition. The compositions typically have pH values of from 6.8 to 11.5. Their pH can be adjusted in the basic range with ammonia. Also, organic amines can be used for this purpose, including monoethanolamine and triethanolamine, or also inorganic bases, such as sodium hydroxide and potassium hydroxide. Inorganic or organic acids can be used for adjusting the pH in the acid range, for example phosphoric acid, acetic acid, citric acid or tartaric acid.

10 The hair coloring compositions of this invention will contain the couplers of this invention, alone or in combination with other couplers, in an effective coloring amount, generally in an amount of from about 0.01 to about 2.5 weight percent. Other couplers, when present will be present in an amount up to about 2.5 weight percent. The primary intermediate(s) will generally be present in an amount of from about 0.01 to about 3.5 weight percent. The molar ratio of primary intermediate to coupler will generally range from about 5:1 to about 1:5 and be employed in any suitable carrier or vehicle, generally an aqueous or hydroalcoholic solution, preferably an aqueous solution.
15 The carrier or vehicle will generally comprise up to about 40 weight percent.
20

25 In order to use the oxidation hair coloring composition for dyeing hair one mixes the above-described hair coloring compositions according to the invention with an oxidizing agent immediately prior to use and applies a sufficient amount of the mixture to the hair, according to the hair abundance, generally from about 60 to 200 grams. Some of the adjuvants listed above (e.g., thickeners, conditioners, etc.) can be provided in the dye composition or the developer, or both, depending on the nature of the ingredients, possible interactions, etc., as is well known in the art.

Typically hydrogen peroxide, or its addition compounds with urea, melamine, sodium borate or sodium carbonate, can be used in the form of a 3 to 12 percent, preferably 6 percent, aqueous solution as the oxidizing agent for developing the hair dye. Oxygen can also be used as the oxidizing agent. If a 6 percent hydrogen peroxide solution is used as oxidizing agent, the weight ratio of hair coloring composition and oxidizing agent is 5:1 to 1:2, but preferably 1:1. The mixture of the oxidizing agent and the dye composition of the invention is allowed to act on the hair for about 10 to about 45 minutes, preferably about 30 minutes, at about 15 to 50°C, the hair is rinsed with water and dried. If necessary, it is washed with a shampoo and eventually after-rinsed with a weak organic acid, such as citric acid or tartaric acid. Subsequently the hair is dried.

The hair coloring composition according to the invention with a compound of formula (1) of this invention as coupler substances permits hair dyeing with outstanding color fastness, especially light fastness, fastness to washing and fastness to rubbing.

In general, a first composition of primary intermediate(s) and coupler(s) is prepared and then, at the time of use, the oxidizing agents, such as H_2O_2 , is admixed therewith until an essentially homogenous composition is obtained which is applied to the hair to be dyed and permitted to remain in contact with the hair for a dyeing effective amount of time, generally for a period of from about 2 to 45, preferably about 2 to 30, minutes, after which the hair is rinsed, shampooed and dried. Optionally, a separate conditioning product may also be provided. Together the hair dye composition of the present invention comprising the hair dye coupler (1) and the developer comprising the oxidizing agent form a system for dyeing hair. This system may be provided as a kit comprising in a single package separate containers of the hair dye compositions, the developer, the optional conditioner or the hair treatment product, and instructions for use.

Example 11

5 The following compositions shown in Table 1 can be used for dyeing Piedmont hair. The dyeing solution is mixed with 100 g 20 volume hydrogen peroxide. The resulting mixture is applied to the hair and permitted to remain in contact with the hair for 30 minutes. This dyed hair is then shampooed and rinsed with water and dried

TABLE 1
Composition for Dyeing Hair

Ingredients	Range (wt %)	Weight (%)
Cocamidopropyl betaine	0-25	17.00
Monoethanolamine ¹	0-15	2.00
Oleic Acid	2-22	0.75
Citric Acid	0-3	0.10
28% Ammonium hydroxide ¹	0-15	5.00
Behentrimonium chloride	1-5	0.50
Sodium sulfite	0-1	0.10
EDTA	0-1	0.10
Erythorbic acid	0-1	0.40
Ethoxydiglycol	1-10	3.50
C11-15 Pareth-9 (Tergitol 15-S-9)	0.5-5	1.00
C12-15 Pareth-3 (Neodol 25-3)	0.25-5	0.50
Isopropanol	2-10	4.00
Propylene glycol	1-12	2.00
P-phenylenediamine ²	0-5	2 mmoles
N,N-Bis(hydroxyethyl)-p-phenylene diamine ²	0-5	2 mmoles
3-Methyl-p-aminophenol ²	0-5	1 mmoles

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p-Aminophenol ²	0-5	5 mmoles
Coupler of this invention	0.5-5	5 mmoles
5-Amino-2-Methyl Phenol	0-5	2 mmoles
2,4-Diaminophenoxyethanol	0-5	2 mmoles
Water	qs to 100.00	qs to 100.00

¹ In the aggregate, these ingredients are in the range of 2 to 15% by weight.

² At least one of these dye precursors is typically present.

Exemplary combinations of hair coloring components employing a coupler compound of formula (1) of this invention are shown in combinations in Table 1 and in C1 to C126 in Table A. Reading down the columns in Table A, the Xes designate the dye compounds (including the novel couplers of the instant invention) that form illustratively suitable combinations of dyes that can be formulated according to the present invention. For example, in Combination No. C1 the novel couplers of the present invention (Row 1 of Table A) with X, R, R¹, R² and R³ are as defined hereinbefore, can be combined with p-toluene diamine and 2-amino-phenol. Especially preferred as the couplers of formula (1) of this invention in the combinations C1 to C126 of Table A are:

1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;
 1-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;
 1-[2-(3-hydroxy-4-hydroxyethyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium chloride;
 1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium bromide;
 1-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl] -3 methyl 3-H-imidazol-1-ium iodide;
 N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;
 N-[2-(3-hydroxy-4-ethyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;
 N-[2-(3-hydroxy-4-hydroxyethyl-phenylamino)-ethyl-N'-methyl-piperidinium chloride;
 N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium bromide; and
 N-[2-(3-hydroxy-4-methyl-phenylamino)-ethyl-N'-methyl-piperidinium iodide.

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Table A.
DYE COMBINATIONS

Structure	IUPAC Name	Name	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15
	3-Hydroxy-4-alkyl-phenylamino-ethyl-1-trialkyl-ammonium halide	3-Hydroxy-4-alkyl-phenylamino-ethyl-1-trialkyl-ammonium halide	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	2-Methyl-benzene-1,4-diamine	p-Toluene-diamine	X	X	X	X	X	X	X	X							
	Benzene-1,4-diamine	p-Phenylene-diamine										X	X	X	X	X	X
	2-[(4-Amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol	N,N-Bis(2-hydroxyethyl)-p-phenylene-diamine															
	4-Amino-phenol	p-Aminophenol															
	4-Amino-3-methyl-phenol	3-Methyl-p-aminophenol															
	2-Amino-phenol	o-Aminophenol	X									X					
	Benzene-1,3-diol	Resorcinol		X									X				
	2-Methyl-benzene-1,3-diol	2-Methyl-resorcinol			X									X			
	Naphthalen-1-ol	1-Naphthol				X									X		
	2-Methyl-naphthalen-1-ol	2-Methyl-1-naphthol					X									X	
	2-(2,4-Diamino-phenoxy)-ethanol	2,4-Diamino-phenoxyethanol						X									X
	Benzene-1,3-diamine	m-Phenylenediamine							X								
	3-Amino-phenol	m-Aminophenol								X							
	5-Amino-2-methyl-phenol	2-Hydroxy-4-aminotoluene									X						
	2-(4,5-Diamino-pyrazol-1-yl)-ethanol	1-Hydroxyethyl-4,5-diamino-pyrazole															

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Table A.
DYE COMBINATIONS

Structure	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
				X	X	X	X	X	X	X	X	X							
	X	X	X										X	X	X	X	X	X	X
				X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
				X									X						
					X									X					
						X									X				
							X									X			
								X									X		
									X									X	
	X									X									X
		X									X								
			X									X							

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Table A...
DYE COMBINATIONS

Structure	C35	C36	C37	C38	C39	C40	C41	C42	C43	C44	C45	C46	C47	C48	C49	C50	C51	C52	C53
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X	X								
	X	X										X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	X	X																	
			X										X						
				X										X					
					X										X				
						X										X			
							X										X		
								X										X	
									X										X
	X									X									
		X									X								

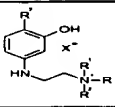
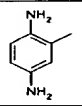
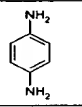
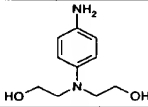
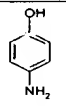
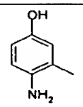
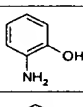
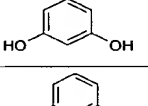
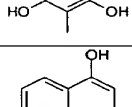
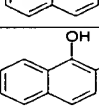
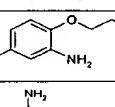
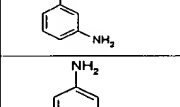
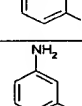
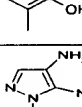
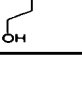

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Table A.
DYE COMBINATIONS

Structure	C54	C55	C56	C57	C58	C59	C60	C61	C62	C63	C64	C65	C66	C67	C68	C69	C70	C71	C72	C73	C74	C75	C76
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	X																						
	X																			x	X	X	X
		x	X	X	X	X	X	X	X	X										x	X	X	X
											x	X	X	X	X	X	X	X	X				
		X									x									x			
			X									X									X		
				X									X									X	
					X									X									X
						X									X								
							X									X							
								X									X						
	X								X									X					
		X								X										X			

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Table A.
DYE COMBINATIONS

Structure	C77	C78	C79	C80	C81	C82	C83	C84	C85	C86	C87	C88	C89	C90	C91	C92	C93	C94	C95	C96	C97	C98	C99
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
															X	X	X	X	X	X	X	X	X
																							
	X	X	X	X	X	X	X	X	X	X	X	X	X	X									
	X	X	X	X	X																		
						X	X	X	X	X	X	X	X	X									
						X									X								
							X									X							
								X									X						
									X									X					
	X									X									X				
		X									X									X			
			X									X									X		
				X									X									X	
					X									X									X
															X	X	X	X	X	X	X	X	X

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Table A.
DYE COMBINATIONS

Structure	C100	C101	C102	C103	C104	C105	C106	C107	C108	C109	C110	C111	C112	C113	C114	C115	C116	C117	C118	C119	C120	C121	C122
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	X	X	X	X	X	X	X	X	X														
											X	X	X	X	X	X	X	X					
																			X	X	X	X	X
	X																		x				
		X																		x			
			X																		x		
				X																		x	
					X																		x
						X																	
							X																
								X															
									X														
	X	X	X	X	X	X	X	X	X	x	x	x	x	x	x	x	x	x	x	x	x	x	x

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Table A.
DYE COMBINATIONS

Structure	C123	C124	C125	C126
	X	X	X	X
	X	X	X	x
	X			
		X		
			X	
				X
	X	X	X	X

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